

# Chemistry

## Lecture 14

By: Syed Ali Shan

### Chemical Equilibrium

#### Outline:

- ✚ Reversible and irreversible reactions
- ✚ State of chemical equilibrium
- ✚ Equilibrium constant expression for important reaction
- ✚ Applications of equilibrium constant
- ✚ Le-Chatelier's principle
- ✚ Synthesis of ammonia by Haber's process
- ✚ Common ion effect
- ✚ Buffer solutions
- ✚ Equilibrium of slightly soluble ionic compounds (solubility product)

#### Chemical Equilibrium

Irreversible Reaction ( $\rightarrow$ )	Reversible Reaction ( $\rightleftharpoons$ )
Takes place in only one direction under standard conditions	Takes place in both directions i.e. forward and reverse under standard conditions
Goes to completion	Never goes to completion
No equilibrium state occurs	Equilibrium state is the ultimate goal
Can be carried out in open as well as in closed container	Only carried out in closed container

#### Chemical Equilibrium:

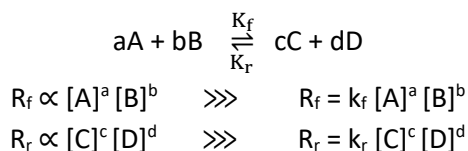
- ❖ State or position of system at which rate of forward reaction is equal to rate of reverse reaction is called dynamic equilibrium
  - It is macroscopic property (deals with molecules in bulk)
  - At start reactant are higher in concentration and concentration decreases as reaction proceeds until becomes constant at equilibrium
  - At start conc. of product is zero, it increases as reaction proceeds until becomes constant at equilibrium
  - Equilibrium can be initiated from either side
  - A catalyst cannot change equilibrium state
  - At equilibrium, concentration of various species remain constant

#### Types of Chemical Equilibrium

- **Homogeneous:** Reactant and Product are in same phase
- **Heterogeneous:** Reactant and Product are in different phase

### Law of Mass Action:

- Rate of reaction (whether forward or reverse) is directly proportional to active masses of reactants (raised to power exponents)
- For dilute solutions; Active masses are equal to concentrations [ ]
- Unit of concentration is mole dm<sup>-3</sup>



- At Equilibrium;

$$R_f = R_r$$
$$k_f [A]^a [B]^b = k_r [C]^c [D]^d$$
$$K_c = \frac{k_f}{k_r} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{[\text{Product}]}{[\text{Reactant}]}$$

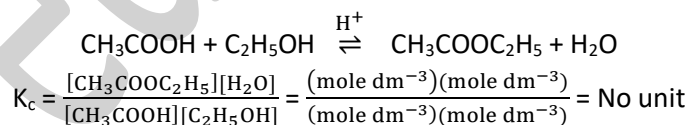
- $k_f, k_r$  are specific rate constants of forward and reverse reactions respectively
- $K_c$  is equilibrium constant

### Features of $K_c$ : (Example.1,3)

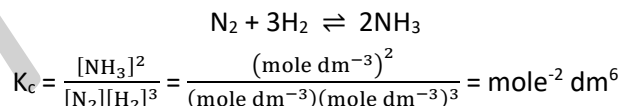
- May or may not have unit
- Independent of concentration, pressure/volume and catalyst
- Affected by temperature, nature of reactants
- $K_c$  is thermodynamic property associated with enthalpy
- In fact all equilibrium constants are only affected by temperature

### Unit of $K_c$ :

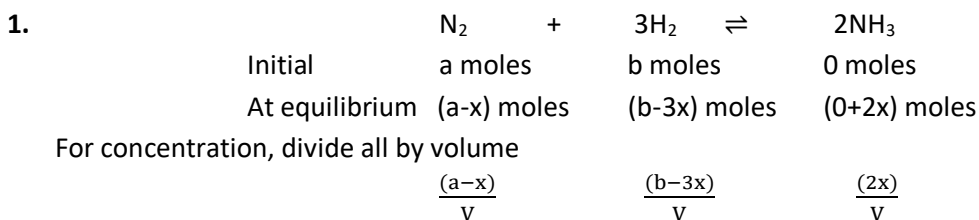
- When  $n_R = n_P$ ,  $K_c$  has no unit



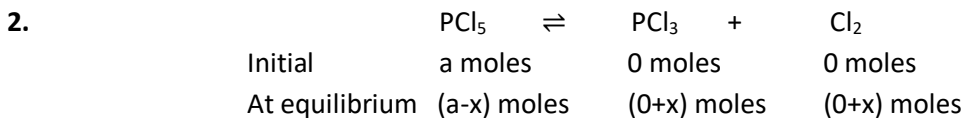
- When  $n_R \neq n_P$ ,  $K_c$  has unit; [(mole dm<sup>-3</sup>)<sup>Δn</sup>]



### $K_c$ Expression for various Reactions: [Q.8, Q.19,20 (for concept)]



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2x/V)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$



For concentration, divide all by volume

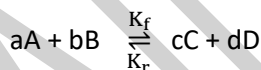
$$\frac{(a-x)}{V} \qquad \qquad \frac{(x)}{V} \qquad \qquad \frac{(x)}{V}$$

$$K_c = \frac{[\text{PCl}_3]^1 [\text{Cl}_2]^1}{[\text{PCl}_5]^1} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{V(a-x)}$$



### Equilibrium Terms:

- ☞  $K_c$  = Equilibrium constant in terms of concentration
- ☞  $K_p$  = Equilibrium constant in terms of partial pressure of gases
- ☞  $K_n$  = Equilibrium constant in terms of no. of moles
- ☞  $K_x$  = Equilibrium constant in terms of mole fraction



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}, K_n = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}, K_x = \frac{X_C^c \times X_D^d}{X_A^a \times X_B^b}$$

### ☞ Relationship b/w $K_c$ & $K_p$ :

$$K_p = K_c (RT)^{\Delta n}$$

$$(\Delta n = n_{\text{product}} - n_{\text{reactant}})$$

1. If  $n_p = n_R \Rightarrow K_p = K_c$
2. If  $n_p > n_R \Rightarrow K_p > K_c$
3. If  $n_p < n_R \Rightarrow K_p < K_c$

**Example#2:**  $\text{N}_2$  and  $\text{H}_2$  combine to give  $\text{NH}_3$ . The value of  $K_c$  in this reaction at  $500^\circ\text{C}$  is  $6.0 \times 10^{-2}$ . Calculate the value of  $K_p$  for this reaction

**Solution:**

$$\begin{aligned} \text{N}_2 + 3\text{H}_2 &\rightleftharpoons 2\text{NH}_3 & (\Delta n = n_p - n_R = 2 - 4 = -2) \\ T = 500 + 273 &= 773 \text{ K} & R = 0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \\ K_p &= 6.0 \times 10^{-2} (0.0821 \times 773)^{-2} \\ K_p &= 1.5 \times 10^{-5} & (K_p < K_c) \end{aligned}$$

### ☞ Applications of $K_c$ :

#### 1. Direction of Reaction:

$$Q_c = \frac{[\text{Product}]}{[\text{Reactant}]}$$

- ☞  $Q_c = K_c \Rightarrow$  Equilibrium state
- ☞  $Q_c > K_c \Rightarrow$  Reverse direction to attain equilibrium
- ☞  $Q_c < K_c \Rightarrow$  Forward direction to attain equilibrium

#### 2. Extent of Reaction:

- ☞  $K_c$  is very large
  - Almost completes in forward direction
 
$$2O_3 \rightleftharpoons 3O_2 \quad K_c = 10^{55} \text{ at } 25^\circ\text{C}$$

$$H_2 + Br_2 \rightleftharpoons 2HBr \quad K_c = 5.4 \times 10^{18} \text{ at } 25^\circ\text{C}$$
  - Reactants are unstable (very less stable) and products are stable
- ☞  $K_c$  is moderate (small)
  - Does not proceed appreciably in forward direction
 
$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad K_c = 10 \text{ at } 25^\circ\text{C}$$

$$CH_3COOH + C_2H_5OH \xrightleftharpoons{H^+} CH_3COOC_2H_5 + H_2O \quad K_c = 4 \text{ at } 25^\circ\text{C}$$

$$N_2O_4 \rightleftharpoons 2NO_2 \quad K_c = 0.36 \text{ at } 25^\circ\text{C}$$
  - Reactants and products are almost equally stable
- ☞  $K_c$  is very small
  - Very little forward reaction
 
$$2HF \rightleftharpoons H_2 + F_2 \quad K_c = 10^{-13} \text{ at } 2000^\circ\text{C}$$

$$N_2 + O_2 \rightleftharpoons 2NO \quad K_c = 1 \times 10^{-30} \text{ at } 25^\circ\text{C}$$
  - Products are unstable (very less stable) and reactants are stable

### 3. The Effect of Conditions on the Position of Equilibrium

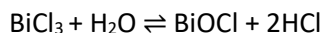
- ☞ Will be discussed in Le-Chatelier's principle

#### Le-Chatelier's Principle

- ✓ If a stress is applied to a system at equilibrium, the system acts in such a way so as to nullify, as far as possible, the effect of that stress
- ✓ Applicable on both physical and chemical changes

#### 1. Effect of change in Concentration:

- ☞ Increase in conc. of reactant or decrease in conc. of product  $\Rightarrow$  Forward
- ☞ Decrease in conc. of reactant or Increase in conc. of product  $\Rightarrow$  Reverse



- Formation of 'BiOCl' (insoluble ppts) makes the solution cloudy
- If we add HCl (product), the reaction moves backwards and we get clear solution
- If we add  $H_2O$  (reactant), the reaction moves forward and we get more cloudy solution

#### 2. Effect of change in Pressure/Volume: (Remember $P \propto \frac{1}{V}$ )

- ☞ Pressure/volume only affects gaseous reactions in which  $n_P \neq n_R$
- ☞ Increase in pressure favours the reaction towards lesser no. of moles (or direction in which moles are decreasing)
- ☞  $2SO_2 + O_2 \rightleftharpoons 2SO_3$  Increase in pressure moves it in forward (as going in forward direction moles are decreasing)

$n_R > n_P$	$n_R < n_P$
Increase in 'P' shifts the reaction forward	Increase in 'P' shifts the reaction backwards
Decrease in 'P' shifts the reaction backwards	Decrease in 'P' shifts the reaction forward

### 3. Effect of change in Temperature:

- In reversible reactions; if reaction is exothermic in forward direction, it will be endothermic in reverse direction or vice versa



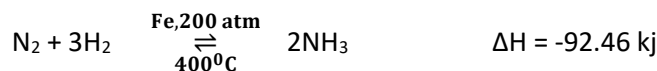
- This reaction will be exothermic in forward direction and so endothermic in reverse direction
- Increase in temperature favours the Endothermic reaction (moves the reaction in direction in which it is endothermic)
- Decrease in temperature favours the Exothermic reaction (moves the reaction in direction in which it is exothermic)
- For endothermic reaction in forward**, increase in 'T' increases rate of reaction, increases the amount of product formed (yield) and  $K_c$  value increases  
Decrease in 'T' decreases rate of reaction and decreases the amount of product formed (yield) and  $K_c$  value decreases
- For exothermic reaction in forward**, increase in 'T' increases rate of reaction, decreases the amount of product formed (yield) and  $K_c$  value decreases  
Decrease in 'T' decreases rate of reaction and increases the amount of product formed (yield) and  $K_c$  value increases
- Effect of 'T' on solubility:**
  - Glucose, sucrose,  $\text{NH}_4\text{Cl}$ ,  $\text{KI}$ ,  $\text{KBr}$  etc have positive enthalpy of solution (endothermic solubility), so increase in 'T' will increase their solubility
  - $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{LiCl}$ ,  $\text{Ce}_2(\text{SO}_4)_3$ ,  $\text{LiBr}$  etc have negative enthalpy of solution (exothermic solubility), so increase in 'T' will decrease their solubility and increase their precipitation
  - Solubility of salts with enthalpy of solution nearly zero or zero is not affected by change in temperature like for  $\text{NaCl}$

### 4. Effect of Catalyst:

- A catalyst neither affects equilibrium position nor equilibrium constant but increases rate of both forward and reverse reactions equally by providing new path (lowering the activation energy)

### Haber's Process for Ammonia Synthesis

- Nitrogen is taken from the air (nearly 13 % nitrogen fixation)
- Hydrogen gas is acquired by burning of natural gas with steam
 
$$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2$$
- Catalyst is 'Fe' embedded in mixture of  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$



- ❖ Equilibrium mixture has 35% by volume ammonia gas
- ❖ Ammonia gas is liquefied and dried with CaO
- ❖ 110 million tons of ammonia are synthesized in world
- ❖ 80 % used for production of fertilizers and some in manufacture of explosives, nylon, other polymers
- ❖ Its yield is maximized by;
  - + Decreasing the temperature
  - + Increasing the pressure
  - + Continuous removal of ammonia



- ❖ Its yield is maximized by;
  - + Decreasing the temperature
  - + Increasing the pressure
  - + Continuous removal of  $\text{SO}_3$

**pH and pOH, Kw, Ka, Kb, pKa pKb:** [only for concept]

- 📖 **pH:** Negative log of hydrogen ion concentration  $\Rightarrow \text{pH} = -\log[\text{H}^+]$
- 📖 **pOH:** Negative log of hydroxide ion concentration  $\Rightarrow \text{pOH} = -\log[\text{OH}^-]$

- 📖 **pH = 7 (neutral)      pH < 7 (acidic)      pH > 7 (basic)**  
 (ionic product of water)  $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$

$$\text{pK}_w = \text{pH} + \text{pOH} = 14$$

$$\text{pK}_a + \text{pK}_b = \text{pH} + \text{pOH} = \text{pK}_w = 14 \quad \text{at } 25^\circ\text{C} \quad (-\log K_a = \text{pK}_a, -\log K_b = \text{pK}_b)$$

**Acidity**  $\propto K_a$  is acid dissociation constant

**Basicity**  $\propto K_b$  is base dissociation constant

$$K_a \propto 1/K_b$$

$$\text{pK}_a \propto 1/\text{strength of acid}$$

$$\text{pK}_b \propto 1/\text{strength of base}$$

**Common ion Effect:**

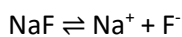
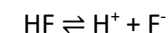
- Suppression of ionization of weak electrolyte by adding a strong electrolyte from outside having common ion
- **Examples:**

$$\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$$

$$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$$
- $\text{Cl}^-$  is the common ion and addition of HCl (strong electrolyte) results the precipitation of NaCl
 
$$\text{NH}_4\text{OH (weak)} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

$$\text{NH}_4\text{Cl (strong)} \rightleftharpoons \text{NH}_4^+ + \text{Cl}^-$$
- $\text{NH}_4^+$  is the common ion and this mixture is used for identification of basic radicals of 3<sup>rd</sup> group
 
$$\text{H}_2\text{S (weak)} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$$

$$\text{HCl (strong)} \rightleftharpoons \text{H}^+ + \text{Cl}^-$$
- $\text{H}^+$  is the common ion and this mixture is used for identification of basic radicals of 2<sup>nd</sup> group



- $\text{F}^-$  is the common ion and addition of NaF (strong electrolyte) results the suppression of HF

### Features of Common ion Effect:

- ✓ It is the application of Le-Chatelier's principle
- ✓ Study the increase in concentration of product in form of common ions
- ✓ Addition of common ion always reverses the direction of reaction for weak electrolyte
- ✓ Term electrolyte is used instead of acid, base or salt
- ✓ Used in purification i.e. purification of NaCl using HCl
- ✓ Used in qualitative analysis (radical identification)
- ✓ Used to prepare Buffers

### Buffer Solutions:

- ❖ The solutions which resist a change in their pH when small amount of acid or base being added
- ❖ Blood is a buffer with pH of 7.35
- ❖ **Acidic Buffer:**
  - Weak acid + its salt (which is made with strong base)
  - $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$  (best buffer when  $[\text{Acid}] = [\text{Salt}]$ )
- ❖ **Basic Buffer:**
  - Weak base + its salt (which is made with strong acid)
  - $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$  (best buffer when  $[\text{Base}] = [\text{Salt}]$ )

### Henderson Equation: [Example 5, Q 23]

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{If } [\text{salt}] = [\text{acid}] \Rightarrow \text{pH} = \text{pK}_a$$

$$\text{If } [\text{salt}] = [\text{base}] \Rightarrow \text{pOH} = \text{pK}_b$$

☞ If  $[\text{salt}]$  is 10 times greater than  $[\text{acid}]$ , then  $\text{pH} = \text{pK}_a + 1$

☞ If  $[\text{salt}]$  is 10 times lesser than  $[\text{acid}]$ , then  $\text{pH} = \text{pK}_a - 1$

**Buffer Capacity:** Capability of buffer to resist the change in its pH

**Solubility:** Amount of solute in 100 g of solvent to make a saturated solution at specific temperature

### Solubility Product (Ksp):

- ❖ Product of the concentrations of ions raised to an exponent equal to the coefficient of the balanced equation
- ❖ For sparingly soluble salts
- ❖ Smaller the value of Ksp, lesser will be the dissociation



$$\text{Ksp} = [\text{A}^{+y}]^x [\text{B}^{-x}]^y$$



$$K_{sp} = [\text{Pb}^{+2}][\text{F}^-]^2$$

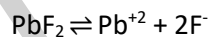
Salt	Ion Product	$K_{sp}$	Salt	Ion Product	$K_{sp}$
AgBr	$[\text{Ag}^+][\text{Br}^-]$	$5.0 \times 10^{-13}$	CuS	$[\text{Cu}^{2+}][\text{S}^{2-}]$	$8 \times 10^{-34}$
$\text{Ag}_2\text{CO}_3$	$[\text{Ag}^+]^2[\text{CO}_3^{2-}]$	$8.1 \times 10^{-12}$	FeS	$[\text{Fe}^{2+}][\text{S}^{2-}]$	$6.3 \times 10^{-18}$
AgCl	$[\text{Ag}^+][\text{Cl}^-]$	$1.8 \times 10^{-10}$	$\text{Fe}_2\text{S}_3$	$[\text{Fe}^{3+}][\text{S}^{2-}]^3$	$1.4 \times 10^{-85}$
AgI	$[\text{Ag}^+][\text{I}^-]$	$8.3 \times 10^{-17}$	$\text{Fe}(\text{OH})_3$	$[\text{Fe}^{3+}][\text{OH}^-]^3$	$1.6 \times 10^{-39}$
$\text{Ag}_2\text{S}$	$[\text{Ag}^+]^2[\text{S}^{2-}]$	$8 \times 10^{-48}$	HgS	$[\text{Hg}^{2+}][\text{S}^{2-}]$	$2 \times 10^{-50}$
$\text{Al}(\text{OH})_3$	$[\text{Al}^{3+}][\text{OH}^-]^3$	$3 \times 10^{-34}$	$\text{MgCO}_3$	$[\text{Mg}^{2+}][\text{CO}_3^{2-}]$	$3.5 \times 10^{-8}$
$\text{BaCO}_3$	$[\text{Ba}^{2+}][\text{CO}_3^{2-}]$	$2 \times 10^{-9}$	$\text{Mg}(\text{OH})_2$	$[\text{Mg}^{2+}][\text{OH}^-]^2$	$6.3 \times 10^{-10}$
$\text{BaSO}_4$	$[\text{Ba}^{2+}][\text{SO}_4^{2-}]$	$1.1 \times 10^{-10}$	MnS	$[\text{Mn}^{2+}][\text{S}^{2-}]$	$3 \times 10^{-11}$
CdS	$[\text{Cd}^{2+}][\text{S}^{2-}]$	$8.0 \times 10^{-27}$	$\text{PbCl}_2$	$[\text{Pb}^{2+}][\text{Cl}^-]^2$	$1.6 \times 10^{-5}$
$\text{CaCO}_3$	$[\text{Ca}^{2+}][\text{CO}_3^{2-}]$	$3.3 \times 10^{-9}$	$\text{PbCrO}_4$	$[\text{Pb}^{2+}][\text{CrO}_4^{2-}]$	$2.3 \times 10^{-13}$
$\text{CaF}_2$	$[\text{Ca}^{2+}][\text{F}^-]^2$	$3.2 \times 10^{-11}$	$\text{PbSO}_4$	$[\text{Pb}^{2+}][\text{SO}_4^{2-}]$	$1.6 \times 10^{-8}$
$\text{Ca}(\text{OH})_2$	$[\text{Ca}^{2+}][\text{OH}^-]^2$	$6.5 \times 10^{-6}$	PbS	$[\text{Pb}^{2+}][\text{S}^{2-}]$	$8.0 \times 10^{-28}$

❖ At least practice relation b/w  $K_{sp}$  and conc. of ions of different salts

#### Applications:

1.  $K_{sp}$  is determined if solubility (S) is given [Example 6, Q.24]
2. Solubility (S) is determined if  $K_{sp}$  is given [Example 7, Q.25]

Relationship b/w  $K_{sp}$  and 'S' is written as when want to find 'S'



$$K_{sp} = (S)(2S)^2 = 4S^3$$